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Impact of delithiated Li_0FePO_4 on the decomposition of $LiPF_6$-based electrolyte studied by accelerating rate calorimetry

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HIGHLIGHTS

- We studied the influence of Li_0FePO_4 on the decomposition of a $LiPF_6$-based electrolyte.
- The study bases on accelerating rate calorimetry (ARC) measurements.
- An inhibiting effect was observed both in the self heating rate and the pressure behaviour.
- The inhibition was independent of the state of charge.
- A reaction hypothesis was formulated based on a detected phase of $Fe_2P_2O_7$ by XRD.

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ABSTRACT

Accelerating rate calorimetry (ARC) was used to investigate the impact of delithiated Li_0FePO_4 on the decomposition of $LiPF_6$-based electrolyte. We used 1 M $LiPF_6$ in a solvent mixture composed of dimethyl carbonate and ethylene carbonate (1:1 w/w). Commercially available $LiFePO_4$-based 18650 lithium-ion cells were completely charged up to a cut-off voltage of 4.2 V and afterwards disassembled in an argon filled glove box. The whole sample preparation for an ARC experiment was carried out under argon atmosphere to prevent atmospheric influences. Beside the self heating rate, we also analysed the pressure rise during an experiment to evaluate the influence of delithiated Li_0FePO_4 on the electrolyte decomposition, which is primarily initiated by the conducting salt $LiPF_6$. The results show both in the self heating rate and the pressure development an inhibiting effect of delithiated Li_0FePO_4 on the electrolyte decomposition. This effect is independent of the state of charge (SOC) and seems to be typical for (delithiated) Li_0FePO_4 in contrast to a commercial $Li[Ni_{0.33}Co_{0.33}Mn_{0.33}]O_2/LiCoO_2$ blend. Besides that, we investigated the thermal behaviour of the bare Li_0FePO_4 and in presence of salt-free solvent. X-ray diffraction after measurements of delithiated Li_0FePO_4 in presence of electrolyte or salt-free solvent showed a new crystalline phase.

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1. Introduction

Lithium-ion batteries have become a promising power source for portable applications and electrical vehicles. Especially transition metal oxide based cathode materials, such as NCM (corresponding to $Li[Ni_{0.33}Co_{0.33}Mn_{0.33}]O_2$) or $LiCoO_2$ are used due to their good electrochemical performance and high capacity resulting in an acceptable high energy density [18,20,21]. However, concerns about the thermal behaviour of these oxide-based cathode materials still exist since oxygen release at higher temperatures can lead to a hazardous combustion reaction driving the flammable alkylcarbonate-based solvent of the electrolyte into fire or explosion. Using C80 microcalorimetry, differential scanning calorimetry (DSC) or accelerating rate calorimetry (ARC), the thermal stability of several lithium-ion cathode materials in contact with solvent and electrolyte was already investigated by many researcher groups, e.g. Refs. [3,10,17]. Among all these cathode materials, $LiFePO_4$ is considered the most promising cathode material with regard to its thermal stability [3,11] and the impossibility to release oxygen at high electrode potentials. The high thermal stability due to the high P═O bonding energy results in comparatively less oxygen release, which reduces the hazard potential of a thermal runaway. Xiang et al. [3] mentioned a suppressive effect of delithiated Li_0FePO_4 on the $LiPF_6$-based electrolyte decomposition by studying the thermal

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behaviour of $LiPF_6$-based electrolyte in contact with various delithiated cathode materials with a C80 calorimeter and also G. Li et al. [7] suspected a possible suppressive effect on the electrolyte decomposition, based on electrochemical impedance measurements of $FePO_4$-coated $LiCoO_2$. But there are also contradictory statements. Ping et al. [2], making thermal investigations based on a C80 microcalorimeter, discussed only a violent decomposition of $LiFePO_4$ in contact with $LiPF_6$-based electrolyte but no inhibiting effect on the electrolyte decomposition, Li et al. [22] observed deposition of electrolyte decomposition products during storage of carbon coated $LiFePO_4$ in contact with electrolyte. It is already well known that the widely used conducting salt $LiPF_6$ decomposes at higher temperatures, to form LiF and the strong Lewis acid PF_5. Especially PF_5 is responsible for a decomposition of the solvent mixture composed of different (di-)alkylcarbonates such as ethylene carbonate (EC), dimethyl carbonate (DMC) or diethylene carbonate (DEC) [4,5,13,19].

The aim of this work was to perform a detailed study of the influence of delithiated Li_0FePO_4 towards a $LiPF_6$-based electrolyte decomposition. Up to now the authors are not aware of any detailed study based on ARC monitoring the impact that delithiated Li_0FePO_4 has on the decomposition of a $LiPF_6$-based electrolyte. In contrast to other groups, we used additionally the information of the pressure rise during an experiment to evaluate the impact of delithiated Li_0FePO_4 on the electrolyte decomposition.

2. Experimental

The cathode material $LiFePO_4$ was obtained from a commercially available cylindrical lithium-ion cell with a nominal capacity of 2 Ah. In order to compare the thermal behaviour with another positive active material, commercial cells containing a cathode material consisting of a NCM/$LiCoO_2$ blend were also investigated (NCM = $Li[Ni_{0.33}Co_{0.33}Mn_{0.33}]O_2$). The cell was charged with a defined current of 1 A to 4.2 V followed by a constant voltage step until the current dropped to 100 mA. Afterwards, the cell was discharged to 2.5 V with the same current. This cycling procedure was repeated three times and ended with a final charging step up to a cut-off voltage of 4.2 V. The fully charged cell was then transferred into an argon-filled glove box and disassembled. The cathode material was scraped from the aluminium collector and rinsed with dimethyl carbonate (DMC) to remove the original electrolyte and possible additives from the surface of the electrode material. Finally, the washed positive electrode material was dried under vacuum for several hours to guarantee that all DMC was removed, before doing any ARC-experiments.

In all experiments the $LiPF_6$-based electrolyte consisted of a solution of 1 M $LiPF_6$ in EC and DMC with a weight ratio of 1:1. This standard solvent mixture was commercially purchased from Merck.

The samples, consisting of the prepared cathode material or a mixture of the cathode material and the standard electrolyte (or salt-free solvent), were placed into a titanium sample holder with a wall thickness of only 0.1 mm. A sample mass of 200 mg of the positive cathode material and 200 mg of the electrolyte were commonly used to carry out the ARC experiments. Since the cathode material was obtained from commercial lithium-ion batteries, the weight of the cathode powder used for the ARC-experiments contains both carbon and binder. The whole sample preparation was made under argon atmosphere to prevent atmospheric influences (especially oxygen and water). All ARC experiments were carried out by an APTAC 254® from Netzsch Gerätebau GmbH (Germany) to evaluate the thermal behaviour of delithiated Li_0FePO_4 in contact with $LiPF_6$-based electrolyte. First of all, the samples were heated to a start temperature of 110 °C. ARC experiments with the electrolyte without any added cathode material were heated up to a starting temperature of 120 °C. Commonly a measurement stopped at 350 °C or when the self heating rate of the sample was higher than 20 °C min^{-1}. Except for the measurements of our pure standard electrolyte and the mixture of electrolyte with the NCM/$LiCoO_2$ blend were applied on an increased shutdown heating rate of 40 °C min^{-1}. In 5 K steps a heat-wait-search procedure (HWS) applied with a waiting time of 15 min before searching for exothermal processes. If no exotherm was found, the temperature was increased with a heating rate of 5 °C min^{-1}. The threshold for an exothermic process was set to a heating rate of 0.02 °C min^{-1}. When the generated heat of our sample exceeded this threshold the following exotherm was monitored under adiabatic conditions. Beside the detection of the temperature and the heating rate generated by our sample, we also recorded the pressure rise during an ARC measurement. This pressure detection delivers additional information about the reaction of delithiated Li_0FePO_4 in presence of $LiPF_6$-based electrolyte, for instance the presence of endothermic reaction. Such endothermic reactions can be assumed if no exothermal process was monitored in the self heating rate but a significant pressure rise deviating from the ideal gas curve was monitored in the same temperature range.

In order to certify the crystalline structure of the delithiated Li_0FePO_4, X-ray diffraction (XRD) was used. The diffractograms were generated in an angle range between 5° and 90° (2θ) by a Bruker-AXS D8 diffractometer equipped with a Bragg–Brentano-optics. XRD was carried out both on the bare positive electrode material after preparation and on the electrode material in presence of the salt-free solvent mixture (EC/DMC (1:1)) or the standard electrolyte after the corresponding ARC experiment.

3. Results and discussion

Fig. 1(a) shows the XRD pattern of $LiFePO_4$ after the charging and rinsing process. As expected, a delithiated phase of $FePO_4$ (=Li_0FePO_4) was predominantly found resulted from the delithiation of the cathode material during charging of the cell.

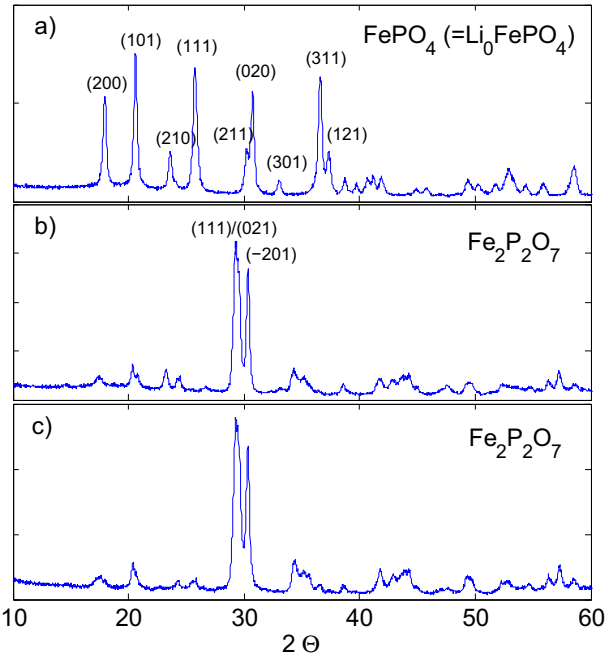

Fig. 1. XRD pattern of 200 mg delithiated Li_0FePO_4: a) After rinsing and drying, b) after an ARC experiment in contact with salt-free solvent (EC/DMC 1:1) and c) after an ARC experiment in contact with the standard electrolyte (1 M $LiPF_6$ in EC/DMC 1:1).

Table 1
Lattice constants for delithiated Li_0FePO_4 and $Fe_2P_2O_7$.

	Li_0FePO_4	$Fe_2P_2O_7$
a (Å)	9.81	6.65
b (Å)	5.79	8.48
c (Å)	4.78	4.49

The XRD pattern shown in Fig. 1(b) and (c) were detected after an ARC experiment of the completely charged $LiFePO_4$ in contact with EC/DMC and the respective standard electrolyte. The corresponding lattice constants are listed in Table 1. The lattice constants of the rinsed and completely delithiated Li_0FePO_4 agree well with those determined by Jiang et al. [1]. The crystalline phase which was mainly found by XRD after an ARC experiment of delithiated Li_0FePO_4 in presence of salt-free solvent or standard electrolyte was $Fe_2P_2O_7$. This phase can be indexed by the strongest diffraction lines at 29° and 30° as shown in Fig. 1(b) and(c). In addition, a small amount of $Li_3Fe_2(PO_4)_3$ was detected when electrolyte or salt-free solvent was presented. We suspect thereby that small amounts of lithiated $LiFePO_4$, which were still presented in the cathode material after charging the battery, could deliver the lithium-ions for the detected phase of $Li_3Fe_2(PO_4)_3$.

First of all, we have investigated the thermal behaviour of the bare and completely charged (delithiated) Li_0FePO_4 without any added solvent or electrolyte. The corresponding ARC experiment showed no exothermic behaviour, whereas an irreversible pressure rise was detected. After reaching the shut down criteria, the experiment cools down to room temperature. The pressure rise is also recorded during cooling down to 50 °C. We denote the pressure at this point as irreversible pressure rise, in case of deviation from the initial pressure (usually 1 bar). Due to the low temperature after cooling down only gaseous reaction products can cause this pressure rise at the end of an experiment. The pressure vs. temperature plot for the bare cathode material is shown in Fig. 2.

After cooling down to 50 °C an irreversible pressure rise of 2.9 bar was detected. This pressure rise might be generated by released oxygen though no exotherm was found. Of course, it cannot be precluded that decomposition or reaction products of the utilized binder [24], which could probably not be removed by our rinsing procedure, have also caused this pressure rise. Jiang et al. [1] assumed an exothermic process starting not till 320 °C, which might be effected by the binder (PVDF) when in contact with delithiated Li_0FePO_4 and solvent (EC/DEC). But in our case the pressure rise mainly occurs below 320 °C and no solvent was presented (only rinsed and dried $FePO_4$). So we expect that the main part of the irreversible pressure rise cannot be caused by binder reactions.

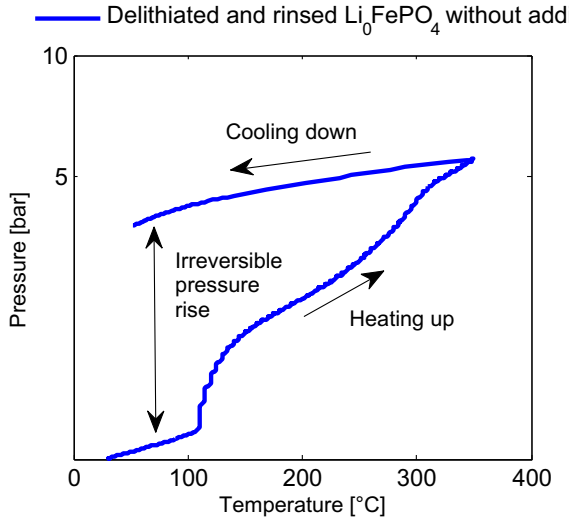

Fig. 2. Pressure vs. temperature plot of 200 mg delithiated Li_0FePO_4 after rinsing with DMC and drying under vacuum.

Chen et al. [6] proposed a decomposition reaction of delithiated $LiMnPO_4$ to $Mn_2P_2O_7$ accompanied by oxygen release after thermal treatment up to 400 °C. $LiMnPO_4$ has an olivine-based structure like $LiFePO_4$. As seen in our XRD analysis, a corresponding crystalline phase of $Fe_2P_2O_7$ was found after ARC experiments of delithiated Li_0FePO_4 in presence of salt-free solvent (EC/DMC) as well as of our standard electrolyte (Fig. 1(b) and (c)). Jiang et al. [11] detected also a new phase of delithiated Li_0FePO_4 after ARC experiments when solvent was presented. But it was not mentioned what kind of crystalline phase was generated. In our case, we expect that the same reduction corresponding to delithiated $LiMnPO_4$ has taken place for delithiated Li_0FePO_4. The corresponding decomposition reaction is shown in Eq. (1).

$$2FePO_4 \rightarrow Fe_2P_2O_7 + \frac{1}{2}O_2. \quad (1)$$

To confirm this reduction mechanism we calculated the standard Gibbs energy ΔG^0. The essential thermodynamic dates were taken from Table 2 corresponding to [26]. Thereby we calculated a value of 3.64 kJ mol^{-1}. $\Delta G^0 > 0$ means firstly a nonvoluntary reduction. Kim et al. [27] studied the temperature phase stability of $FePO_4$ by XRD and detected a growth of the $Fe_2P_2O_7$ XRD peaks starting at 600 °C. But in this case no addition of solvent or electrolyte was used. Ong et al. [28] presented in his work an analysis of thermal reduction of delithiated $MnPO_4$ and $FePO_4$ based on the quarternary phase diagrams making the simplifying assumption that the reaction entropy is dominated by the oxygen entropy since most phase equilibria changes in these systems are solid state reactions involving oxygen release or absorption. The work confirms a much lower critical oxygen chemical potential μ_{O_2} of −1.72 eV for $FePO_4$ compared to −0.83 eV for $MnPO_4$ resulting in a much higher reduction temperature around 700 °C for $FePO_4$. Both works confirm a high reduction temperature for $FePO_4$. But in our case the phase of $Fe_2P_2O_7$ was detected in presence of salt-free solvent or our standard electrolyte after ARC experiments running up to 350 °C. We speculate thereby that especially our salt-free solvent works as a reducing agent leading to a decreased reduction temperature.

Before studying the reaction behaviour with $LiPF_6$-based electrolyte, we have investigated the reaction between the delithiated Li_0FePO_4 in contact with the salt-free solvent EC/DMC. If oxygen is released, we assume that the reactivity between delithiated Li_0FePO_4 and solvent can be considered as a simple oxidation of the solvent. After that, we made an ARC experiment with the corresponding standard electrolyte (1 M $LiPF_6$ in EC/DMC (1:1)). Consequently, the only varied parameter between these two experiments was finally the addition of 1 M $LiPF_6$. Fig. 3 shows the resulting self-heating rate vs. temperature plots. In case of the reaction behaviour between delithiated Li_0FePO_4 and the solvent, we have found an onset temperature at 250 °C with a maximum

Table 2
Standard thermodynamic functions at 298.15 K for $FePO_4$ and $Fe_2P_2O_7$ [26].

Function	$FePO_4$	$Fe_2P_2O_7$
ΔS^0 (J mol^{-1} K)	119.20	220.50
ΔH^0 (kJ mol^{-1})	18.345	32.963
ΔG^0 (kJ mol^{-1})	17.194	32.779

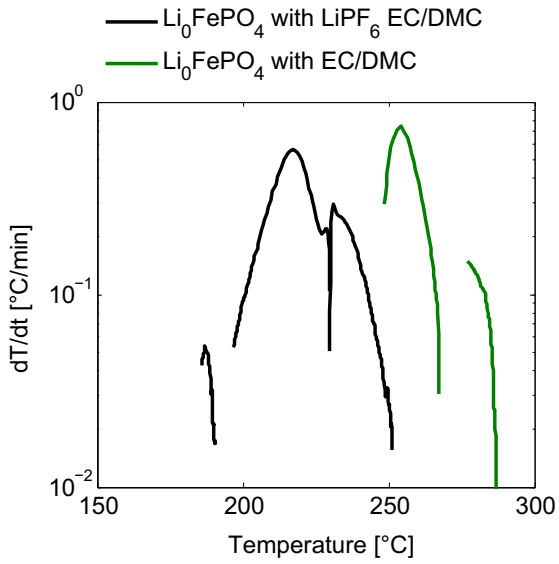

Fig. 3. Self heating rate vs. temperature plot of 200 mg delithiated Li_0FePO_4 in contact with 200 mg solvent (EC/DMC 1:1) and also 200 mg electrolyte (1 M $LiPF_6$ in EC/DMC 1:1).

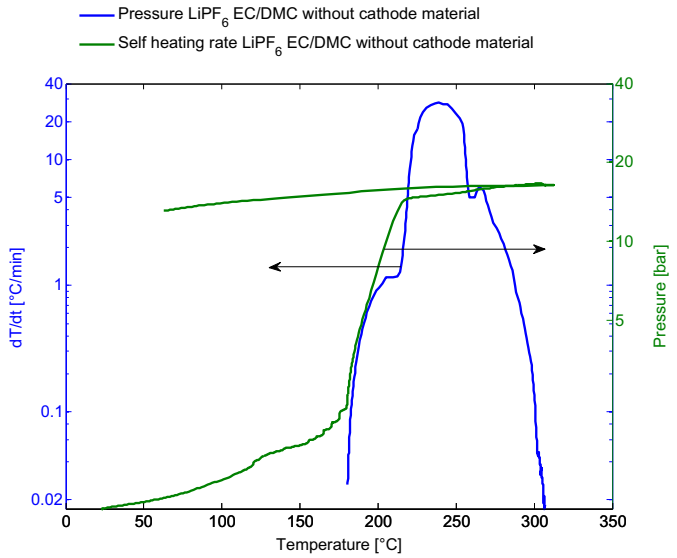

Fig. 4. Self heating rate (SHR) and pressure vs. temperature plot of 200 mg of the standard electrolyte (1 M $LiPF_6$ in EC/DMC 1:1).

heating rate below 1 °C min^{-1}. We suspect that this exothermic signal might be caused by an oxidation of the solvent coupled to the released oxygen of the $FePO_4$ decomposition as described previously. The exotherm cannot be caused only by the solvent. ARC measurement of the solvent itself showed no exothermic behaviour, but an irreversible pressure rise (not shown), possibly generated by endothermic decomposition products. Due to the low heating rate (under 1 °C min^{-1}), the amount of released oxygen can only be quite small in case of an oxidation process. This can be ascribed to the strong covalent P=O bond with a high bonding energy of 5.64 eV [12], making $FePO_4$ thermally stable [8].

In contrast, the ARC measurements with addition of the standard electrolyte containing 1 M $LiPF_6$ showed an onset temperature already at 200 °C with a weaker exotherm at 185 °C. However, like the measurement of delithiated Li_0FePO_4 in presence of the salt-free solvent, the maximum heating rate does not exceed 1 °C min^{-1}. From Fig. 3, we can see that delithiated Li_0FePO_4 has a good safety behaviour in contact with alkylcarbonate-based solvent and $LiPF_6$-based electrolyte. This safety behaviour of $LiFePO_4$, as compared to other commercial transition metal oxide-based cathode materials, like delithiated $Li_{0.5}CoO_2$ or $Li[Ni_{0.33}Co_{0.33}Mn_{0.33}]O_2$ (see e.g. Refs. [9,10]), is already well known [11,23]. But, as Jiang and Dahn [1] showed, we can conclude that the exotherm around 200 °C is caused only by the conducting salt $LiPF_6$, since the signal does not appear when no $LiPF_6$ (only salt-free solvent) is present (see Fig. 3). Further on, it can be seen that the exothermic signal of the salt-free solvent in contact with delithiated Li_0FePO_4 disappears when $LiPF_6$ is added. In this case, reaction products caused by the conducting salt $LiPF_6$ might inhibit the oxygen release.

Fig. 4 shows the thermal behaviour of the standard electrolyte without cathode material. In the same plot we can see the corresponding pressure rise of the standard electrolyte. The main pressure rise takes place between 180 °C and 220 °C. The corresponding exothermic processes are primary caused by the ring opening reaction of EC followed by a polymerization reaction [5]. Responsible for this reaction mechanism is the strong Lewis acid PF_5, which is generated by the reversible endothermic decomposition (see Eq. (2)) of the conducting salt $LiPF_6$ [4,5]. Ping et al. [2] found a melting (T_m = 200 °C [25]) and decomposition heat for $LiPF_6$ of 29.3 and 430 J g^{-1}, respectively.

$$LiPF_{6(s)} \rightleftharpoons LiF_{(s)} + PF_{5(g)} \quad (2)$$

Such endothermic processes have no influence on the self heating rate generated with an ARC, but they influence the pressure detection. Therefore, Fig. 5 compares the pressure rise of the electrolyte and the salt-free solvent. The electrolyte shows no exothermic behaviour between room temperature and 180 °C. In addition, we can see the approximated ideal gas expansion curve according to Eq. (3). p_{init} describes the pressure and T_{init} the temperature at the beginning of the measurement. Assuming that at the beginning of an experiment only argon is present in the gas phase, Eq. (3) describes the expansion of argon under ideal gas conditions.

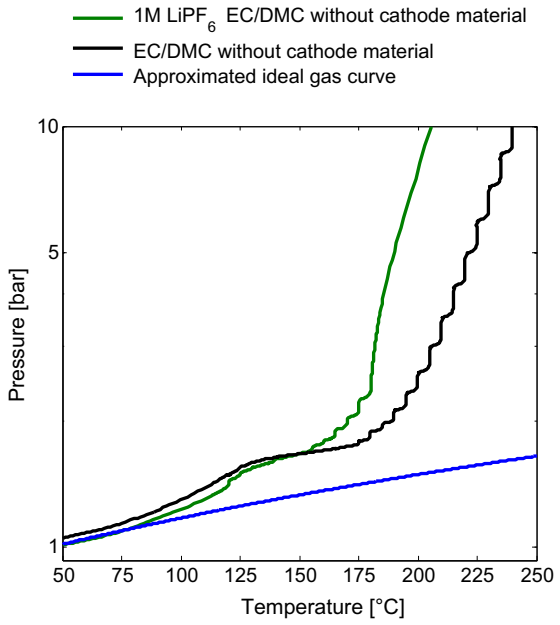

Fig. 5. Deviation of the pressure rise of 200 mg baseline electrolyte (1 M $LiPF_6$ in EC/DMC 1:1) and solvent EC/DMC 1:1 from an approximated ideal gas curve.

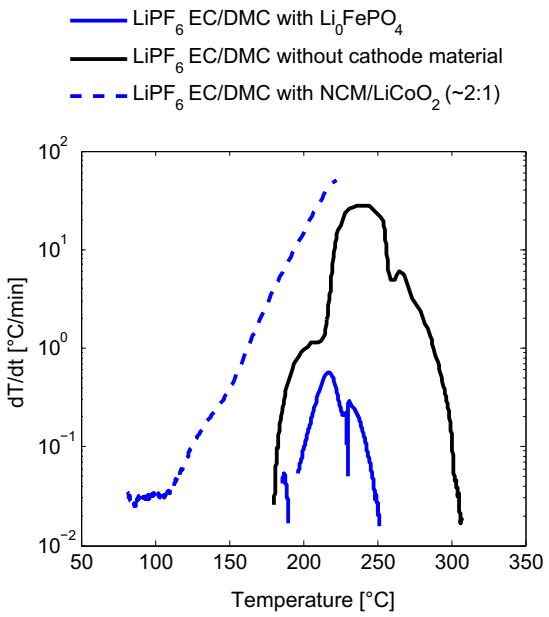

Fig. 6. Self heating rate vs. temperature plot of 200 mg delithiated Li_0FePO_4 and 200 mg NCM/$LiCoO_2$, respectively, in presence of 200 mg standard electrolyte and 200 mg of the standard electrolyte without cathode material.

$$p = p_{\text{init}} \cdot \frac{T}{T_{\text{init}}} \tag{3}$$

At around 85 °C we observe a deviation from the ideal gas curve. It can be seen that this deviation can only be caused by the solvent. At around 160 °C we observe a deviation of the pressure rise of the standard electrolyte from the corresponding salt-free solvent. Since no exothermic signal was detected at this temperature for the electrolyte (see Fig. 4), an endothermic process must be responsible. We assume thereby, that this enhanced pressure deviation is finally generated by the decomposition of the conducting salt $LiPF_6$, forming PF_5 according to Eq. (2). Ping et al. [2] made thermal investigations on a $LiPF_6$ based electrolyte with a C80 microcalorimeter and observed in the same temperature range an endothermic process. Considering the pressure behaviour of the electrolyte and the solvent in our measurements, respectively, without any addition, it can be concluded that an enhanced decomposition of $LiPF_6$ starts at around 160 °C and initiates the exothermic processes of the electrolyte observed at 180 °C accompanied with an exothermic pressure rise. As Roth et al. [29] already mentioned, these results confirm a critical gas generation onset temperature of around 160 °C leading to venting of lithium ion cells. After all, we should not neglect the pressure rise caused by the vaporization of the salt-free solvent as seen in Fig. 5.

Fig. 6 shows the exothermic signals of the delithiated Li_0FePO_4 in presence of our standard electrolyte and again the self heating rate of the standard electrolyte itself. The self heating rate for both ARC experiments stopped at certain temperatures and decreased for higher temperatures.

The $LiPF_6$-based electrolyte without any addition has an onset temperature at 180 °C and a maximum heating rate of 28 °C min^{-1}. The same qualitative thermal behaviour of a $LiPF_6$-based electrolyte after ARC experiments was detected by Gnanaraj et al. [13]. In contact with delithiated Li_0FePO_4 the heating rate is lowered under 1 °C min^{-1} (corresponding to a reduction factor of nearly 30) and the onset temperature shifts to 185 °C. Since the exothermic behaviour of delithiated Li_0FePO_4 in presence of the electrolyte, starting at 185 °C, can only be caused by $LiPF_6$, we have to assume a clear inhibition of the thermal decomposition of $LiPF_6$-based electrolyte in contact with delithiated Li_0FePO_4. For comparison Fig. 6 shows in addition the experiment of another commercial cathode material, composed of a NCM/$LiCoO_2$ blend, in contact with the standard electrolyte. Compared to $LiFePO_4$ the NCM/$LiCoO_2$ blend showed no inhibiting effect. The heating rate progress of the commercial NCM/$LiCoO_2$ blend in contact with our standard electrolyte would lead to a thermal runaway.

Fig. 7 shows again the thermal analysis of the delithiated Li_0FePO_4 in presence of the electrolyte, whereby three different state of charges (SOC) were previously adjusted. We investigated the state of charge values 100% (already shown in Fig. 6), 80% and 50%. The maximum heating rates for SOC 80% and 50% are still under 1 °C min^{-1}. Since there is no increase in the heating rate or a significant shift in the onset temperature towards a lower temperature, within measuring accuracy of our apparatus, the inhibiting effect of delithiated Li_0FePO_4 is essentially independent of the state of charge and thus of the degree of delithiation.

This inhibiting effect is not only evident by the self heating rate. Fig. 8 shows the pressure rise vs. time plot due to exothermal

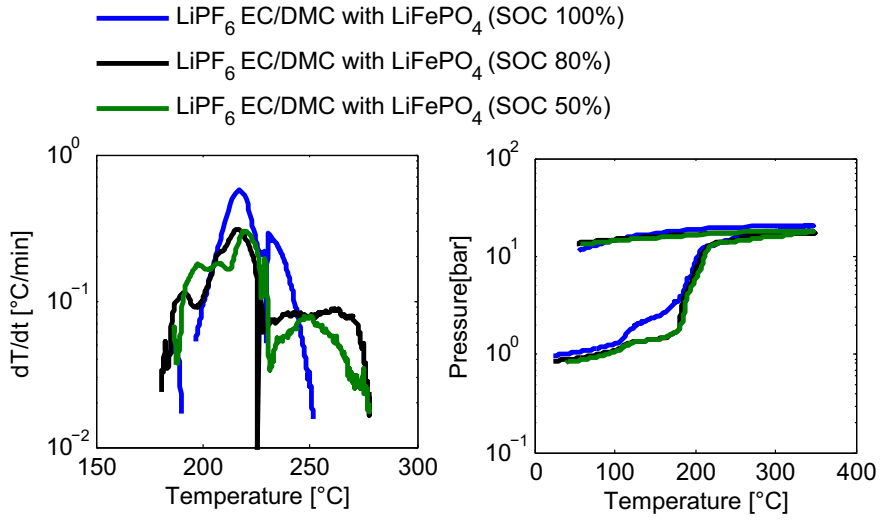

Fig. 7. a) Self heating rate vs. temperature plot of 200 mg $LiFePO_4$ at different state of charges (SOC 50%, 80% and 100%) respectively in contact with 200 mg electrolyte, b) corresponding pressure vs. temperature plot.

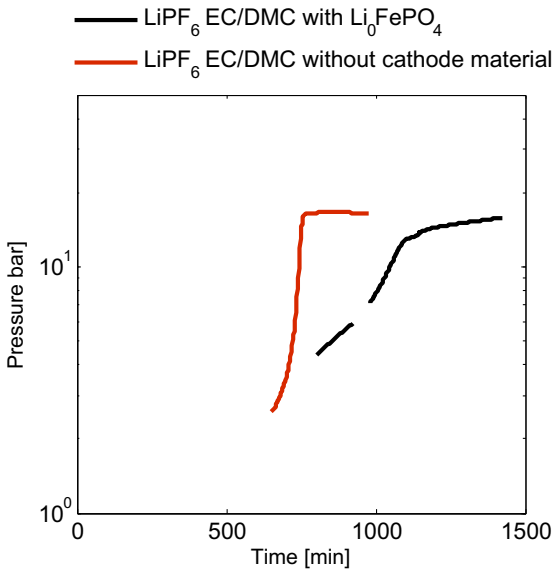

Fig. 8. Pressure rise vs. time plot due to exothermal processes of 200 mg of the electrolyte without addition and also in contact with delithiated Li_0FePO_4.

reactions. The main exothermal pressure rise caused by the $LiPF_6$-based electrolyte takes nearly 200 min, whereas the sample electrolyte plus delithiated Li_0FePO_4 is delayed up to 350 min. Further on, it can be seen that the exothermal pressure increase is lowered when delithiated Li_0FePO_4 is added to the standard electrolyte.

Considering finally the obtained and discussed results of the self heating rates and pressure rises of the electrolyte itself and the electrolyte in contact with delithiated Li_0FePO_4, an inhibiting effect of delithiated Li_0FePO_4 on the electrolyte decomposition was clearly distinguished detected. As proposed by Xiang et al. [3], there might be active PO_4^{3-} species adsorbing the active Lewis acid PF_5, which is finally responsible for the decomposition of $LiPF_6$-based electrolytes. To understand this behaviour in detail further studies have to be done. But reflecting again the detected phase of $Fe_2P_2O_7$ by XRD after ARC experiments, as described at the beginning of the work, we formulate the following reaction hypothesis:

$$2FePO_4 \rightarrow Fe_2P_2O_7 + \frac{1}{2}O_2 \tag{4}$$

$$PF_5 \rightarrow PF_3 + F_2 \tag{5}$$

$$PF_3 + \frac{1}{2}O_2 \rightarrow PF_3O \tag{6}$$

$$2FePO_4 + PF_5 \rightarrow Fe_2P_2O_7 + F_2 + PF_3O \tag{7}$$

Apart from all that, it can be excluded that the suppression of the heating rate is only caused due to heat absorption by the cathode material. Therefore we considered the so called ϕ-factor according to Eq. (8):

$$\phi = \frac{C_{p,\text{total}}}{C_{p,\text{sample}}} = \frac{C_{p,\text{electrolyte}} + C_{p,\text{cathode}} + C_{p,\text{clip}} + C_{p,\text{container}}}{C_{p,\text{electrolyte}} + C_{p,\text{cathode}}} \tag{8}$$

with

$$C_{p,i} = c_{p,i} \cdot m_i. \tag{9}$$

The used heat capacity values $c_{p,i}$ are listed in Table 3. The heat capacity for delithiated Li_0FePO_4, the sample container (titanium) and the clip (copper) were estimated by the Dulong Petit law [14], whereas values of the electrolyte were taken from literature [15,16]. As the salt does not change $C_{p,\text{electrolyte}}$ much, we used the same values for electrolyte solution and salt-free solvent. This resulting ϕ-factor describes the ratio between the heat capacity of the total system and that one of the samples considering only the cathode material and electrolyte. The ϕ-factor is used to define the sensitivity of an ARC measurement. A value near 1.0 would be optimal, but is often not feasible. A ϕ-factor of 1.5 can be seen as very good. In our ARC experiments, the ϕ-factor for the measurement of 200 mg of delithiated Li_0FePO_4 in contact with 200 mg electrolyte was 1.7 and that one of 200 mg electrolyte itself without cathode material was 2.2. Assuming that $FePO_4$ does not generate heat (only the electrolyte does) and behaves like the sample holder or the clip, we have calculated an adapted ϕ-factor based on Eq. (10):

$$\phi = \frac{C_{p,\text{total}}}{C_{p,\text{sample}}} = \frac{C_{p,\text{electrolyte}} + C_{p,\text{cathode}} + C_{p,\text{clip}} + C_{p,\text{container}}}{C_{p,\text{electrolyte}}}. \tag{10}$$

Table 3
Calculated heat capacities used for the calculation of the ϕ-factor (see Eqs. (8) and (10)).

Component	Material	Heat capacity $c_{p,i}$ (J g^{-1} K^{-1})
Sample container	Titanium (m = 0.65 g)	0.52
Clip	Copper (m = 0.185 g)	0.39
Cathode	Lithium iron phosphate $LiFePO_4$	1.1
Solvent	Ethylene carbonate (EC)	1.52
Solvent	Dimethyl carbonate(DMC)	1.83
Solvent	EC/DMC 1:1	1.67

Fig. 9 shows the self heating rate of 100 mg, 150 mg and 200 mg electrolyte itself without cathode material and additionally the self heating rate of delithiated Li_0FePO_4 in presence of 200 mg of the electrolyte. The calculated ϕ-factor values are also shown in Fig. 9. First of all we can see, that a reduction of 50 mg electrolyte causes a decrease of the maximum heating rate of about the triple fold for

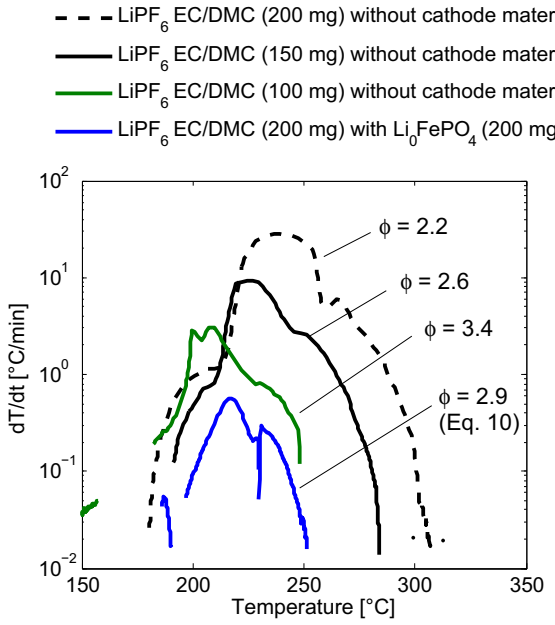

Fig. 9. Self heating rate vs. temperature plot of 200 mg, 150 mg and 100 mg of the $LiPF_6$-based electrolyte and also 200 mg of the $LiPF_6$-based electrolyte in contact with delithiated Li_0FePO_4.

the experiments of the electrolyte without cathode material. The measurement of 100 mg of our standard electrolyte without any addition has a higher ϕ-factor as the experiment of the cathode material and 200 mg added standard electrolyte. This means a lower sensitivity. Nevertheless, we have a three times higher maximum heating rate (3 °C min^{-1} compared to under 1 °C min^{-1}). Consequently, the reactivity has to be higher though an inferior ϕ-factor value and a lower amount of electrolyte. Consequently, an inhibiting effect should be responsible for the reduction of the heating rate shown in Fig. 6 and not only heat absorption due to the addition of 200 mg solid $FePO_4$.

4. Conclusion

The results in this work obtained by ARC confirm first and foremost, both by considering the self heating rate and the pressure behaviour, an inhibiting effect of delithiated Li_0FePO_4 on the exothermal $LiPF_6$-based electrolyte decomposition. This inhibiting effect is independent of the state of charge and an inhibited heating rate due to heat absorption by the solid phase consisting of Li_0FePO_4 in our sample can be precluded by considering the ϕ-factor as a measure for the sensitivity of an ARC experiment. Our observations underline the good safety behaviour of $LiFePO_4$ as cathode material for lithium ion batteries. Besides that we could show that $LiPF_6$-based electrolyte leads to a decomposition of delithiated Li_0FePO_4 at lower temperatures compared to the bare cathode material during thermal abuse. Based on this result we formulated a possible reaction hypothesis.

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